



# Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron

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## ABSTRACT

The pre-treatment of a pharmaceutical wastewater (PWW) by Fenton oxidation with zero-valent iron (ZVI) and hydrogen peroxide was investigated to improve the degradation of the complex-mixture of organic compounds present in the wastewater. The influence of different crucial parameters such as the initial hydrogen peroxide concentration, the ZVI concentration and the capacity of the ZVI/H<sub>2</sub>O<sub>2</sub> system to treat different organic loading have been evaluated. The optimal conditions for degradation led to TOC reductions of up to 80% in only 1 h of treatment. This degree of organic mineralization was reached by using moderate loadings of ZVI and hydrogen peroxide (ZVI/TOC weight and H<sub>2</sub>O<sub>2</sub>/TOC molar ratios of 12 and 3.2, respectively). Moreover, the use of waste-metallic iron shavings in terms of TOC removal compared to commercial ZVI powder may be a promising and cheaper development.

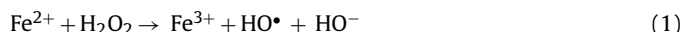
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## 1. Introduction

In the treatment of pharmaceutical wastewaters, it has always been troublesome to achieve stringent effluent standards due to the wide variety of products produced in the drug manufacturing plant [1–3]. These effluents are characterized by high BOD and COD values and low BOD/COD ratios with variable concentrations of salts. They comprise pharmaceuticals and hormonally active substances which are very refractory to common conventional treatments (i.e. biological, physical and chemical methods). Recently, those compounds have been detected in different aquatic environmental sources as a result of hospital and industrial discharges and due to their very stable refractory behavior in the conventional operations of the sewage treatment plants. Nowadays, the study of the adverse effects of pharmaceutical compounds on living organisms is giving rise to a growing concern [4].

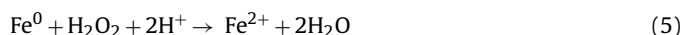
Advanced oxidation processes, have been found to be successful for the abatement of refractory and/or toxic organic pollutants in water and wastewater, being mostly used in combination with conventional biological and chemical methods [5,6]. In the last years, Fenton's process (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) is considered as an industrially viable alternative operating at room conditions of pressure and temperature and the reagent components are easy to handle with. This system promotes the formation of highly reactive hydroxyl

radicals, according to Eq. (1), able to oxidize a wide range of compounds [7]:



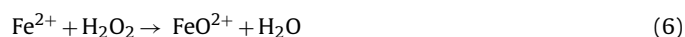
The main drawback of this technology is related to the high amount of ferrous iron salts needed (usually FeSO<sub>4</sub>), which must be separated from the treated effluent (generally by precipitation) leading to considerable loads of iron-containing sludge that will require further management [8,9].

Lately, an alternative Fenton system has been studied that involves the oxidation of zero-valent iron (ZVI) at acidic conditions generating in situ Fe<sup>2+</sup>, Eq. (2), which promote the generation of hydroxyl radicals (Eq. (1)). The main advantage of this alternative is the use of ZVI commercial heterogeneous material instead of the common iron salts usually used in conventional Fenton processes [10–12]. Moreover, a fast recycling of ferric iron into ferrous species at the metal surface can take place following Eq. (3). Zero-valent iron (ZVI) has been used for the degradation of different model pollutants. ZVI oxidation by dissolved oxygen produces H<sub>2</sub>O<sub>2</sub> via a two-electron transfer from the particle surface to oxygen (Eq. (4)). The H<sub>2</sub>O<sub>2</sub> produced is either reduced to water (Eq. (5)) or converted to HO<sup>•</sup> or Fe (IV) (e.g. FeO<sup>2+</sup>) by reaction with Fe (II) (Eqs. (1) and (6), respectively) [13]:



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However, investigations into ZVI applications for industrial wastewater, with high mixed-organic load content, have so far been limited. In any case, those Fenton-like ZVI processes have been successfully applied on the treatment of several wastewaters such as textile industries wastewaters [14] or landfill leachate [15] using different types of ZVI.

The aim of this work is to assess the feasibility of the ZVI/H<sub>2</sub>O<sub>2</sub> technology on the depuration of a real industrial wastewater generated from a pharmaceutical manufacturing plant in Spain, as a complementary process on its existing treatment plant. The influence of different crucial parameters in the Fenton-like ZVI process such as the initial hydrogen peroxide, the ZVI concentration and the capacity of the ZVI/H<sub>2</sub>O<sub>2</sub> system for the treatment of wastewaters at different organic loading have been evaluated. Furthermore, in order to minimize the operating costs, besides testing commercially available ZVI powder, the application of iron shavings obtained from metallurgical residues have also been assessed.

## 2. Materials and methods

### 2.1. Reagents

Iron metal powder (Sigma–Aldrich, 97% pure) and hydrogen peroxide (Scharlab, 30% pure) were used as purchased. Iron shavings were obtained from discarded material from a metallurgical manufacturing process.

### 2.2. Experimental procedures

In a typical experimental set-up, a cylindrical glass vessel was filled with 200 mL of the pharmaceutical wastewater (PWW). The PWW was previously diluted 1/100 until an initial TOC of 0.1 g L<sup>-1</sup>, unless otherwise specified. Thereafter, appropriate amounts of hydrogen peroxide and zero-valent iron were added in the presence of aeration with a flow rate of 5 L min<sup>-1</sup>. The temperature was controlled at 22 ± 2 °C during the reaction. The iron metal was suspended in the aqueous solution and gently mixed using a magnetic stirrer while adjusting the pH to 3 with H<sub>2</sub>SO<sub>4</sub>. The influence of the initial hydrogen peroxide concentration was studied for H<sub>2</sub>O<sub>2</sub>/TOC molar ratios of 0.8, 1.6 and 3.2 (corresponding to half of the stoichiometric amount (0.230 g L<sup>-1</sup>), the stoichiometric amount (0.460 g L<sup>-1</sup>) or twice the stoichiometric amount (0.920 g L<sup>-1</sup>) of the oxidant). Likewise, the concentration of zero-valent iron was studied using 0.6, 1.2 and 2.4 g L<sup>-1</sup>.

Samples were taken throughout the reaction time (0, 10, 20, 40 and 60 min) and filtered through 0.22 μm nylon membranes prior to analysis. Total organic carbon (TOC) content of the samples was determined using a combustion/non-dispersive infrared gas analyzer model TOC-V (Shimadzu). Hydrogen peroxide concentration was measured by iodometric titration and the iron content in the filtered solution after reaction was measured by ICP-AES analysis using a Varian Vista AX spectrometer. The pH of the solution was measured using a Metrohm pH meter.

## 3. Results and discussion

### 3.1. Characterization of the pharmaceutical wastewater

The drug manufacturing plant located in Madrid (Spain) is dedicated to producing active pharmaceutical compounds framed in the families of antibiotic, anti-ulcer, anti-depressant and anti-hypercholesterolemic compounds. The annual production of the pharmaceutical plant is around 300 tons through different production sections: a fermentation plant, two extraction units and

**Table 1**

Physicochemical characteristics of the PWW.

PWW	
pH	9.75 ± 0.01
TOC (mg L <sup>-1</sup> )	10,021 ± 1327
COD (mg L <sup>-1</sup> )	49,620 ± 9758
BOD <sub>5</sub> (mg L <sup>-1</sup> )	3754 ± 653
Total nitrogen (mg N L <sup>-1</sup> )	285 ± 7
Nitrites (mg L <sup>-1</sup> )	0.5 ± 0.1
Nitrates (mg L <sup>-1</sup> )	16.0 ± 2.8
Sulphates (mg L <sup>-1</sup> )	891 ± 143
Conductivity (μS cm <sup>-2</sup> )	16,835 ± 219
Turbidity (NTU)	51 ± 1

four areas of chemical synthesis and semi-synthesis. The wastewater streams, coming from the chemical (20–25%) and biological (75–80%) processes are collected in a homogenization tank. The existing treatment removes volatile solvents by stripping and adds ferric sulphate as a highly cationic flocculant for the removal of suspended solids and the partial reduction of the organic matter. The resultant effluent is finally treated by a secondary biological treatment (activated sludge with pure oxygen).

Table 1 shows the physico-chemical characteristics of the studied industrial wastewater taken from the homogenization tank. The wastewater sample contains a high organic content of 10 g L<sup>-1</sup> in terms of TOC and a BOD<sub>5</sub>/COD ratio of 0.076, which indicates a low biodegradability. It is also noteworthy the high conductivity which reveals the presence of high contents of inorganic salts.

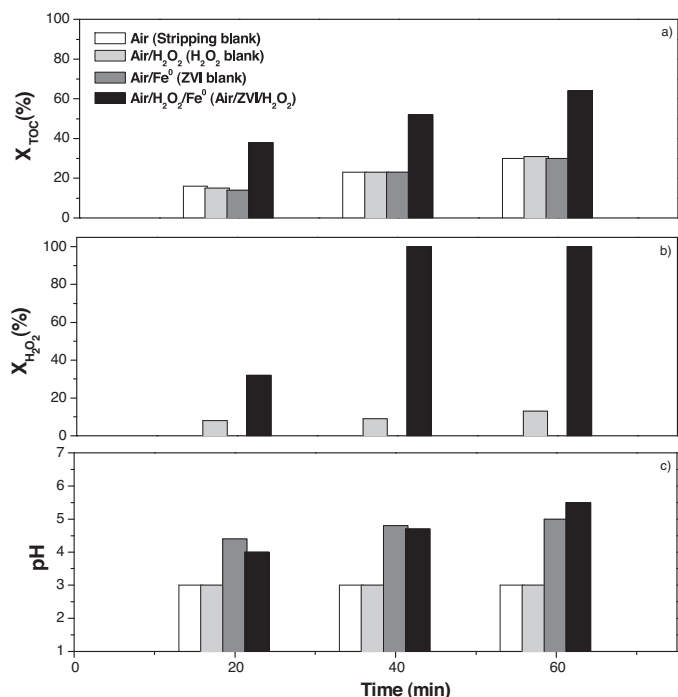
### 3.2. Preliminary experiments to determinate the efficiency of aerated ZVI/H<sub>2</sub>O<sub>2</sub> systems

The efficiency of the aerated ZVI/H<sub>2</sub>O<sub>2</sub> system (air/ZVI/H<sub>2</sub>O<sub>2</sub>) for the treatment of pharmaceutical wastewater samples of TOC 0.1 g L<sup>-1</sup> was firstly studied. This system was evaluated by comparing the catalytic performance of the Air/ZVI/H<sub>2</sub>O<sub>2</sub> system with several blank experiments: (i) only aeration (air), in order to evaluate the possible stripping of the volatile pollutants, (ii) aeration in the presence of ZVI without H<sub>2</sub>O<sub>2</sub>, in order to evaluate the oxidizing power of the Air/ZVI system, and (iii) aeration in the presence of H<sub>2</sub>O<sub>2</sub> without ZVI, in order to determine the oxidizing potential of H<sub>2</sub>O<sub>2</sub> in a non-catalytic system (air/H<sub>2</sub>O<sub>2</sub>). Fig. 1 shows the TOC and hydrogen peroxide conversions, as well as the pH values for the above-mentioned experiments.

The aerated blank experiment in the absence of H<sub>2</sub>O<sub>2</sub> and ZVI revealed a significant reduction of the TOC content with a 24% removal after 60 min (Fig. 1a). This fact evidences the removal of a significant proportion of volatile organic compounds contained in the PWW by stripping.

It was remarkable that not significant differences were obtained in terms of the TOC conversions between the aerated blank experiments using hydrogen peroxide (air/H<sub>2</sub>O<sub>2</sub>) or ZVI (air/ZVI). These results demonstrated a negligible effect of the hydrogen peroxide as oxidant and the ZVI alone under aerated conditions for the treatment of the wastewater, unlike the promising results reported in literature for the air/ZVI system in the degradation of model pollutants [16,17]. The combination air/ZVI/H<sub>2</sub>O<sub>2</sub> though, showed a remarkable increase in terms of TOC conversions, achieving 38% and 65% after 20 and 60 min, respectively. Therefore, it is clear the significant role of both ZVI and H<sub>2</sub>O<sub>2</sub> together in the reaction system.

With regards to the conversion of the oxidant (Fig. 1b), the hydrogen peroxide conversion was completely consumed after 40 min in the air/ZVI/H<sub>2</sub>O<sub>2</sub> system. In the case of the air/H<sub>2</sub>O<sub>2</sub> experiment, the oxidant conversion only reached 13% after 60 min,



**Fig. 1.** TOC (a) and hydrogen peroxide (b) conversions and pH (c) of blank and catalytic air/ZVI/ $\text{H}_2\text{O}_2$  systems. Initial experimental conditions:  $\text{TOC}_0$   $0.1 \text{ g L}^{-1}$ , acidic pH (3), ZVI ( $1.2 \text{ g L}^{-1}$ ),  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio 1.6 and air flow ( $5 \text{ L min}^{-1}$ ).

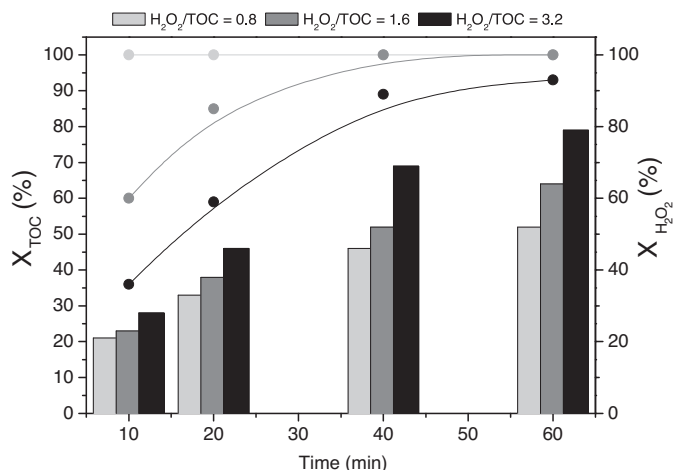
which is in agreement with the low TOC conversion achieved in the absence of the ZVI catalyst.

The results of pH (Fig. 1c) clearly showed that in all the experiments where the ZVI catalyst was not present (air and air/ $\text{H}_2\text{O}_2$ ), the initial pH kept constant throughout time, with values of 3 after 60 min. However, in the presence of zero-valent iron (air/ZVI and air/ZVI/ $\text{H}_2\text{O}_2$ ) the pH increased over time, from the initial value of 3–5.6 after 60 min. Note that as the pH increased, the ferryl iron ions can be formed and are stable, either in the bulk solution or on the catalyst surface. These species could keep oxidizing the intermediates and thus justifying the increase in the TOC conversion observed even when the hydrogen peroxide was depleted [18–21]. This is particularly evident in the air/ZVI/ $\text{H}_2\text{O}_2$  system where the TOC conversion increased from 52 to 64% in the last 20 min of reaction in the absence of hydrogen peroxide. Therefore, this may indicate the presence of oxidizing species such as ferryl iron (e.g.  $\text{FeO}^{2+}$ ).

### 3.3. The effect of the initial $\text{H}_2\text{O}_2$ dosage

The effectiveness of the Fenton-like ZVI treatment depends on the formation of oxidizing species such as hydroxyl radicals, which are produced by the decomposition of the hydrogen peroxide. The influence of different  $\text{H}_2\text{O}_2$  dosages within the range of  $0.23$ – $0.96 \text{ g L}^{-1}$  (corresponding to  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 0.8, 1.6 and 3.2) was studied for the treatment of PWW containing  $0.1 \text{ g L}^{-1}$   $\text{TOC}_0$  using  $1.2 \text{ g L}^{-1}$  of ZVI and initial pH of 3.

Fig. 2 shows the results of the TOC and hydrogen peroxide conversions using different hydrogen peroxide concentrations for the treatment of PWW. The increase of the hydrogen peroxide evidenced a clear enhancement of performance reaching values up to 80% TOC conversions when the highest oxidant loading ( $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 3.2) was employed. It is well known that when one of the Fenton reactants ( $\text{Fe}^{2+}$  or  $\text{H}_2\text{O}_2$ ) is overdosed, it can react with the hydroxyl radicals inhibiting the organic degradation [8]. An excess of oxidant induces the radical scavenging reaction



**Fig. 2.** The effect of hydrogen peroxide concentrations ( $\text{H}_2\text{O}_2/\text{TOC}$  molar ratios 0.8, 1.6 and 3.2) in terms of TOC (columns) and hydrogen peroxide (points) conversions. Initial experimental conditions:  $\text{TOC}_0$   $0.1 \text{ g L}^{-1}$ , acidic pH (3), ZVI ( $1.2 \text{ g L}^{-1}$ ) and air flow ( $5 \text{ L min}^{-1}$ ).

(Eq. (7)). However, such inhibition was not observed using  $1.2 \text{ g L}^{-1}$  of ZVI under the studied hydrogen peroxide dosage range.

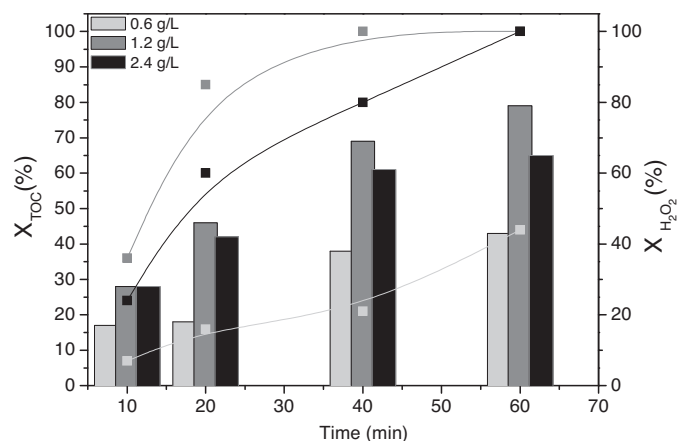


Regarding the hydrogen peroxide conversions, a reasonable decreasing was observed as the oxidant concentration increased keeping the ZVI concentration constant. Total oxidant consumptions were achieved after 10 and 40 min of treatment for the  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratios of 0.8 and 1.6, respectively. Interestingly, the TOC degradation continued even after the consumption of the initial  $\text{H}_2\text{O}_2$ . This fact is partly attributed to the oxidation of ZVI under aerated conditions to produce hydrogen peroxide (Eq. (4)) but the main mechanism is probably the oxidizing role of the ferryl ions species, as it is known that these species may be formed at pHs close to neutral and can act as oxidants [17]. This is supported by the fact that the pH tended toward neutral values of 5.3–5.5 as the reaction progressed. Additionally, the formation of iron oxides on the metallic ZVI surface has been reported in literature as another mechanism that could generate hydroxyl radicals due to the formation of galvanic cells between ZVI and the iron oxides formed on the ZVI surface [22]. The formation of iron oxides supported on the metallic iron surface is plausible as the pH of the reaction medium increased, which would also reduce the presence of the iron species in the treated aqueous solution. In fact, the iron concentration in the all three experiments hardly showed significant variations ( $13.7$ ,  $13.1$  and  $12.4 \text{ mg L}^{-1}$  for  $\text{H}_2\text{O}_2/\text{TOC}$  of 0.8, 1.6 and 3.2, respectively), which is probably due to the similar pH value obtained of the treated aqueous solutions after 60 min.

### 3.4. The effect of the initial ZVI concentration

The decomposition performance of the Fenton peroxidation is mainly determined by the availability of ferrous ions, which have a major role in the formation of hydroxyl radicals. Therefore, the influence of the ZVI concentration as a precursor of ferrous ions, due to the corrosion of the metallic surface, was investigated. Fig. 3 shows TOC and hydrogen peroxide conversions of experiments performed for the treatment of PWW containing  $0.1 \text{ g L}^{-1}$   $\text{TOC}_0$  using all three ZVI concentrations ( $0.6$ ,  $1.2$  and  $2.4 \text{ g L}^{-1}$ ) and a  $\text{H}_2\text{O}_2/\text{TOC}$  molar ratio of 3.2.

These results evidenced the enhancement of the TOC conversions as the ZVI concentration increased from  $0.6$  to  $1.2 \text{ g L}^{-1}$ . However, a TOC decrease was observed when ZVI concentration



**Fig. 3.** The effect of ZVI concentration on the degradation of the PWW in terms of TOC (columns) and H<sub>2</sub>O<sub>2</sub> (points) conversions. Initial experimental conditions: TOC<sub>0</sub> 0.1 g L<sup>-1</sup>, acidic pH (3), H<sub>2</sub>O<sub>2</sub>/TOC molar ratio 3.2 and air flow (5 L min<sup>-1</sup>).

increased to 2.4 g L<sup>-1</sup>. A maximum TOC conversion of 80% was achieved using 1.2 g L<sup>-1</sup> of ZVI after 60 min of treatment. As it was mentioned, ZVI provides ferrous ions to the bulk solution (Eq. (2)), which participate and catalyze the decomposition of hydrogen peroxide to produce hydroxyl radicals (Eq. (1)). Therefore, the increase of ZVI loading can accelerate the generation rate of hydroxyl radicals, but an excess of iron could also reduce the degradation performance [14] since excessive reductive ZVI could also promote the decomposition of hydrogen peroxide toward non-reactive oxygen species and the scavenging of hydroxyl radicals (Eqs. (5) and (8), respectively).

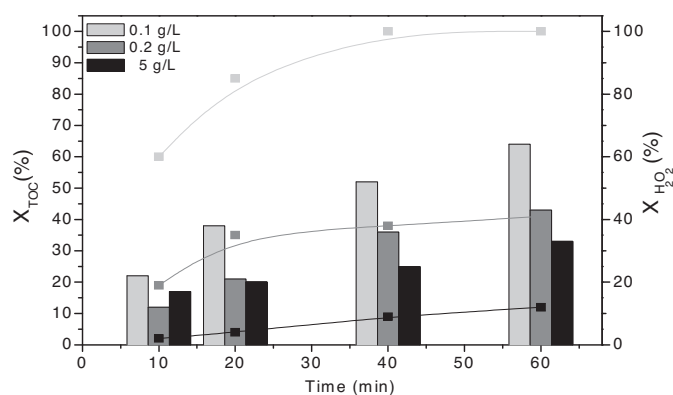


The increase of TOC conversion when the ZVI loading increased from 0.6 to 1.2 g L<sup>-1</sup> was also accompanied by an increase of the hydrogen peroxide conversion. The oxidant consumption was low when using ZVI 0.6 g L<sup>-1</sup> (7, 16, 21 and 24% after 10, 20, 40 and 60 min, respectively), whereas using 1.2 g L<sup>-1</sup> the hydrogen peroxide conversion increased from 36% at 10 min to 85% after 20 min, obtaining a total consumption after 40 min. Likely, the decrease of TOC conversion for 2.4 g L<sup>-1</sup> of ZVI was also reflected by the decrease of the hydrogen peroxide consumption (25, 60, 80 and 100% after 10, 20, 40 and 60 min of reaction, respectively). It was also noted that the increase of pH toward neutral values during the reaction time was getting higher as the ZVI concentration increased. After 60 min of reaction, the pH increased from 3 to 3.4, 4.9 and 5.3 for 0.6, 1.2 and 2.4 g L<sup>-1</sup> of ZVI, respectively. These results were associated to the production of OH<sup>-</sup> by the Fenton reaction (Eq. (1)) and to the scavenging of hydroxyl radicals by ferrous ions (Eq. (8)).

The TOC increase in the case of optimum ZVI amount (1.2 g L<sup>-1</sup>) when hydrogen peroxide was depleted confirmed a different mechanism of TOC degradation driven probably by the oxidizing power of the ferryl ions species. Strong evidences suggest that the nature of the oxidants formed in ZVI systems depends on the pH of the solution, varying from hydroxyl radical at low pH to another reactive oxidant species, such as the ferryl ions, at around neutral pH values [16].

### 3.5. The effect of the initial TOC concentration of the pharmaceutical wastewater

The aim of these experiments was to evaluate the feasibility of the Fenton-like ZVI system for the treatment of more concentrated samples of the PWW. Then, the effects of different 1/100, 1/50 and



**Fig. 4.** The effect of initial TOC loadings of 0.1, 0.2 and 5 g L<sup>-1</sup> in terms of TOC (columns) and H<sub>2</sub>O<sub>2</sub> (points) conversions. Initial experimental conditions: acidic pH (3), ZVI (1.2 g L<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub>/TOC molar ratio 1.6 and air flow (5 L min<sup>-1</sup>).

1/2 dilutions, using 1.2 g L<sup>-1</sup> of ZVI and a H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 1.6 are shown in Fig. 4.

Remarkable degradations were obtained for the treatment of the pharmaceutical wastewater diluted 1/100, reaching values of 22, 38, 52 and 64% after 10, 20, 40 and 60 min of reaction, respectively. When the initial TOC increased to 0.2 g L<sup>-1</sup> (dilution 1/50), the TOC conversions decreased obtaining a final TOC conversion of 43% after 60 min. The increase of the initial TOC concentration until 5 g L<sup>-1</sup> showed also a reduction of the TOC conversion reaching 33% at the end of the reaction. Therefore, the efficiency of the Fenton-like ZVI system was significantly affected by the increase of the initial organic loading of the pharmaceutical wastewater.

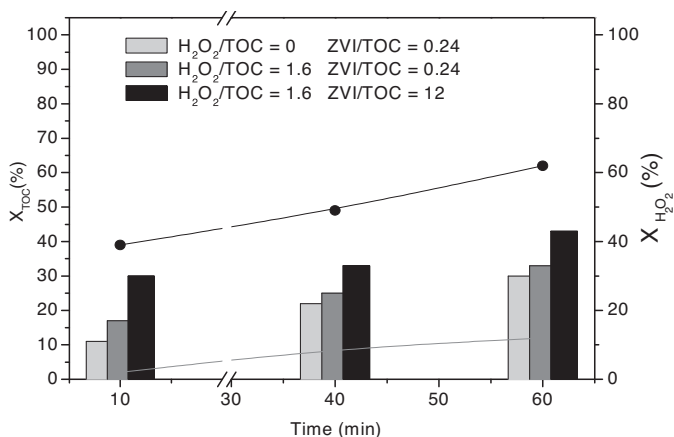
It was also observed a decrease in the hydrogen peroxide conversion by increasing the initial TOC concentration. Thus, a hardly 12% H<sub>2</sub>O<sub>2</sub> was consumed when using 5 g L<sup>-1</sup> initial TOC after 60 min, increasing up to 41% and 100% for 0.2 g L<sup>-1</sup> and 0.1 g L<sup>-1</sup> initial TOC, respectively. These results are likely associated to the deactivation of the ZVI catalyst due to the decrease of the ZVI/TOC weight ratio as the initial TOC concentration increases (12, 6 and 0.24 for 0.1, 0.2 and 5 g L<sup>-1</sup>, respectively).

The inactivation of the surface seems to be related to a less accentuated increase of the pH, which would be indicating a lower contribution of the ferrous ions in the typical Fenton reaction for the production of HO<sup>•</sup> and HO<sup>-</sup> (Eq. (1)). In the systems with initial 0.2 and 5 g L<sup>-1</sup> TOC, the pH increased quite slightly reaching a maximum value of 3.8 and 3.7, respectively compared to value of 5.5 obtained when using initial TOC of 0.1 g L<sup>-1</sup>. Also, lower TOC conversions were obtained compared to the treatment of 0.1 g L<sup>-1</sup>, being the hydrogen peroxide still present throughout the reaction time.

It was also attested a decrease of the H<sub>2</sub>O<sub>2</sub> conversion for the experiment performed using 5 g L<sup>-1</sup> as compared to the 0.1 g L<sup>-1</sup> PWW sample (Fig. 4). This fact seemed to confirm a less effective role of the Fenton-like ZVI system for the treatment of a more concentrated pharmaceutical wastewater effluent as a consequence of the partial passivation of the ZVI surface.

In order to evaluate the effect of the ZVI/TOC weight ratio on the application of the Fenton-like ZVI system for the treatment of high concentrated pharmaceutical wastewater samples (initial TOC 5 g L<sup>-1</sup>), an additional experiment was carried out increasing the ZVI/TOC ratio. Fig. 5 shows the TOC and hydrogen peroxide conversions of experiments performed for the treatment of 5 g L<sup>-1</sup> PWW with a H<sub>2</sub>O<sub>2</sub>/TOC molar ratio 1.6 and ZVI/TOC ratio 0.24 and 12. The results of the treatment carried out using a ZVI/TOC ratio 0.24 without hydrogen peroxide are also shown.

The comparison of air/ZVI.0.24 and air/ZVI/H<sub>2</sub>O<sub>2</sub>.0.24 indicated the role of the hydrogen peroxide, although this effect for the



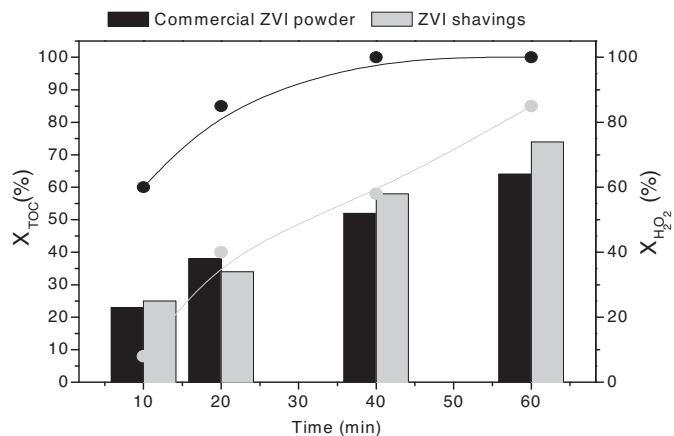
**Fig. 5.** The effect of ZVI/TOC ratio on the treatment of 5 g L<sup>-1</sup> PWW in terms of TOC (columns) and H<sub>2</sub>O<sub>2</sub> (points) conversions. Initial experimental conditions: acidic pH (3), H<sub>2</sub>O<sub>2</sub>/TOC molar ratio of 1.6 and air flow (5 L min<sup>-1</sup>).

treatment of the high concentrated PWW (5 g L<sup>-1</sup> TOC) was less significant than that shown for the diluted PWW sample (0.1 g L<sup>-1</sup> TOC) shown in Fig. 1. The air/ZVI/H<sub>2</sub>O<sub>2</sub>-12 system showed a TOC enhancement reaching 45% after 60 min of reaction. However, it was lower than the 65% obtained in the treatment of the diluted PWW of 0.1 g L<sup>-1</sup> (using in both cases the same ZVI/TOC weight and H<sub>2</sub>O<sub>2</sub>/TOC molar ratios).

### 3.6. Application of iron shavings

Metal shavings generated in the manufacturing process of a metallurgical industry were used and compared to the commercial powder ZVI. The use of this waste material makes the Fenton-like ZVI system very attractive from the economic and environmental points of view. Therefore, the degradation efficiency of both types of ZVI for the treatment of the diluted PWW 0.1 g L<sup>-1</sup> TOC was studied using 1.2 g L<sup>-1</sup> of ZVI and a H<sub>2</sub>O<sub>2</sub>/TOC molar ratio 1.6.

Fig. 6 shows TOC and H<sub>2</sub>O<sub>2</sub> conversions obtained for the commercial powder ZVI and the waste metallic iron shavings. The latest reached TOC conversions of 25, 34, 58 and 75%, over 10, 20, 40 and 60 min of reaction, respectively, revealing a slightly increase compared to the results observed for the commercial ZVI powder under



**Fig. 6.** The effect of the ZVI source in terms of TOC (columns) and hydrogen peroxide (points) conversions. Initial experimental conditions: TOC<sub>0</sub> 0.1 g L<sup>-1</sup>, acidic pH (3), ZVI (1.2 g L<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub>/TOC molar ratio 1.6 and air flow (5 L min<sup>-1</sup>).

the same experimental conditions (22, 38, 52 and 64% over 10, 20, 40 and 60 min, respectively). It was also shown a lower H<sub>2</sub>O<sub>2</sub> consumption for the iron shavings with final H<sub>2</sub>O<sub>2</sub> conversion of 85% unlike the total oxidant conversion obtained after 40 min when using ZVI powder.

## 4. Conclusions

This study shows that the air/ZVI/H<sub>2</sub>O<sub>2</sub> system can be considered as an effective alternative solution for the removal of many organic pollutants present in wastewater generated from a drug manufacture plant. TOC reductions of up to 80% were obtained in only 1 h of treatment, signifying an easy, economic and effective pre-treatment step. H<sub>2</sub>O<sub>2</sub>/TOC molar ratios of 0.8, 1.6 and 3.2 were studied, evidencing a clear enhancement of performance when the highest oxidant loading was employed. Likewise, the enhancement of the TOC conversions was also observed as the ZVI concentration increased from 0.6 to 1.2 g L<sup>-1</sup>, but decreased when ZVI concentration increased to 2.4 g L<sup>-1</sup>, as excessive reductive ZVI could also promote the decomposition of H<sub>2</sub>O<sub>2</sub> toward non-reactive oxygen species and the scavenging of the hydroxyl radicals.

It must be noted that the optimal organic mineralization degree (up to 80%) was reached by using moderate loadings of ZVI and hydrogen peroxide (ZVI/TOC weight and H<sub>2</sub>O<sub>2</sub>/TOC molar ratios of 12 and 3.2, respectively). Moreover, the use of waste-metallic iron shavings instead of commercial ZVI powder, showed very promising results and further work on delineating the mechanisms are currently ongoing. The treatment of concentrated pharmaceutical wastewater by this air/ZVI/H<sub>2</sub>O<sub>2</sub> system however, was less efficient than the use of more dilute effluents.

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